Redox oxides-based solar thermochemistry and its materialization to reactor/heat exchanger concepts for efficient solar energy harvesting, transformation and storage

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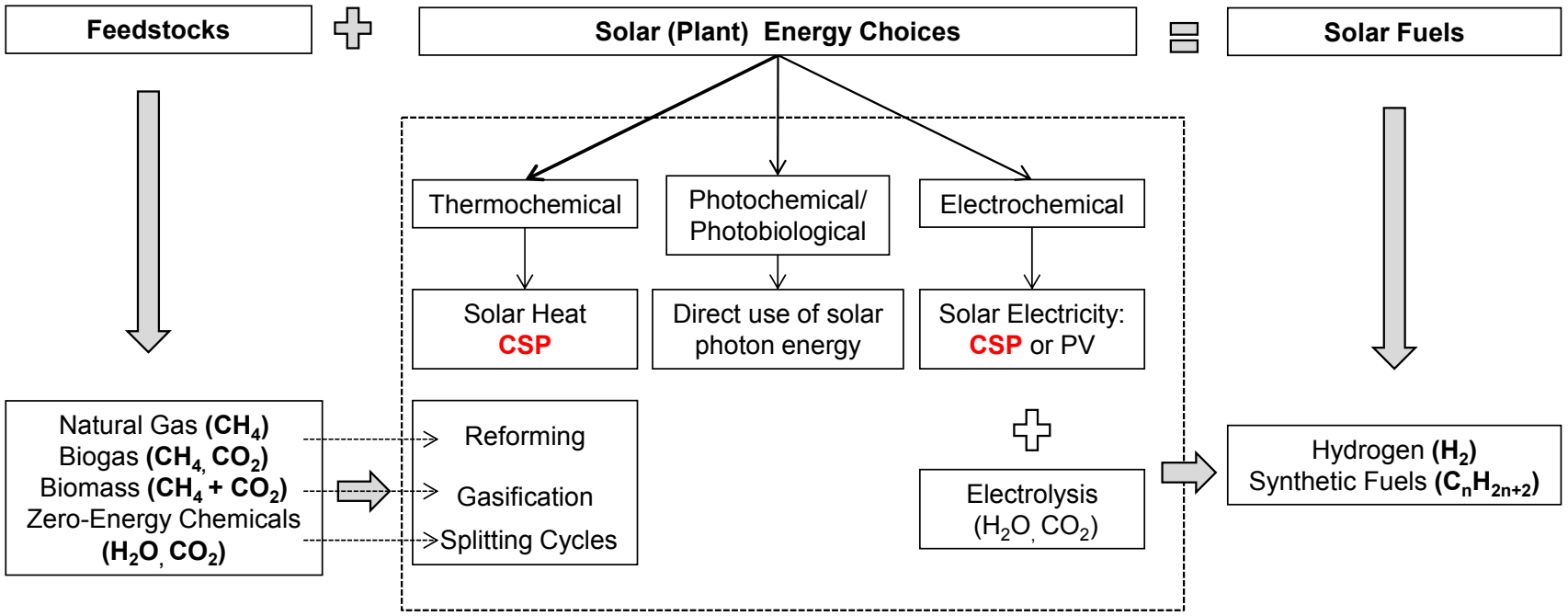
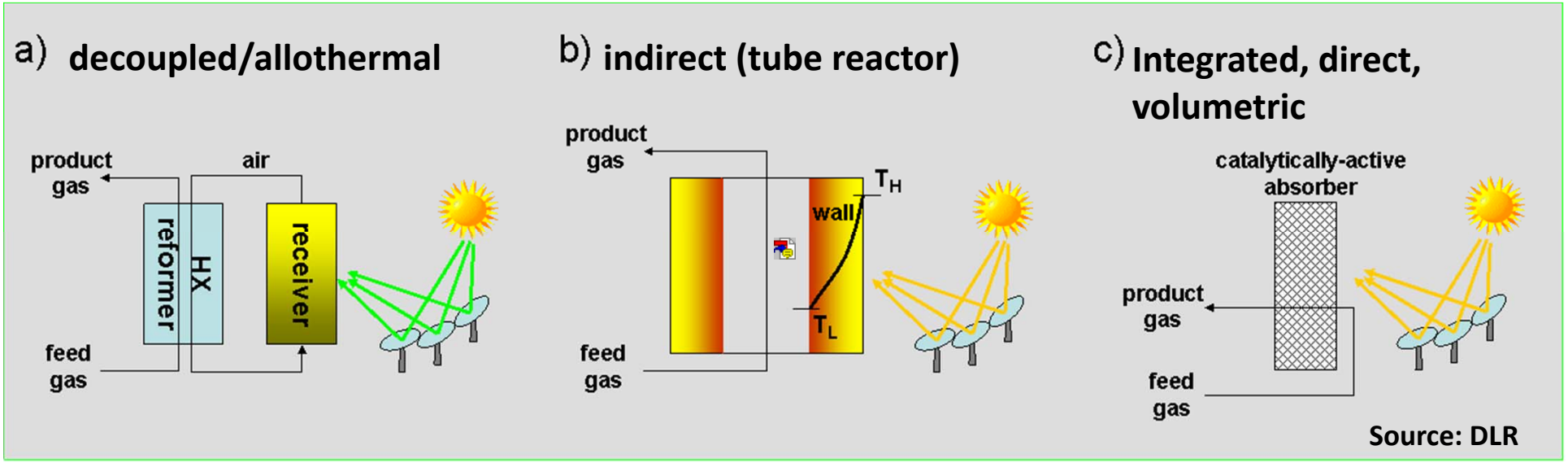
Introduction

- Solar fuels production from Concentrating Solar Systems and Solar Thermal Power Plants (STPPs)
- Solar fuels chemistries and reactors
- Commonalities in materials requirements and reactor concepts among solar energy conversion, storage and transformation-related processes.
- Outlook, needs and ideas for the future.

Partial listing of various feedstocks and solar energy variances for solar liquid hydrocarbon fuels production



Solar Methane Reforming– Reformer (heating) Technologies



Reformer heated externally (700 to 850°C)

E.g. **ASTERIX** project

Irradiated reformer tubes (up to 850°C), temperature gradient

Development: Australia, Japan; Research in Germany and Israel

Catalytic active direct irradiated absorber

DLR coordinated projects: **SOLASYS, SOLREF**; Research in Israel, Japan

Reforming vs. W/CD redox-oxides-"splitting" Chemistry

- Employs fossil fuel (CH_4) as reactant.
- Solid catalyst: Ni-based catalysts supported on $CaAl_6O_{10}$ or $MgAl_2O_4$; noble metals (Ru, Rh, Pd, Pt); Fe, Co.

- Temperature range: **700-850°C.**
- Gaseous reactants can be fed **continuously.**

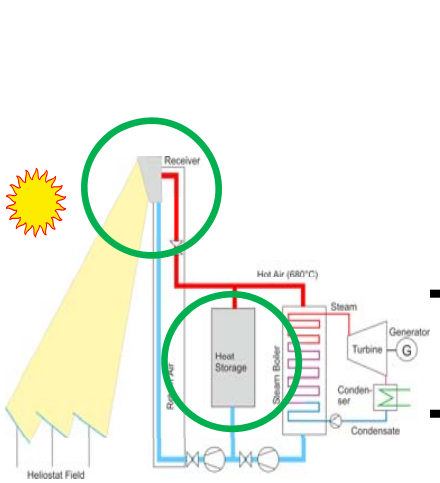
- Employs **CO_2 as a reactant**; i.e. can "reuse/valorize" atmospheric CO_2.
- Solid redox–pair materials: ferrites ($NiFe_2O_4$, $CoFe_2O_4$), CeO_2-ZrO_2, perovskites ($La_{1-x}Sr_xMn_yAl_{1-y}O_{3-\delta}$).
- Temperature range: 750-1500°C.
- Solid is not a "catalyst" but a reactant, with non-negligible mass to be heated to the reaction temperature and progressively depleted during reaction, having to be replenished (reactions cannot be carried out continuously).

Reforming vs. W/CD "splitting" solar reactors

- Structured reactors.
- Solar heating: direct or indirect.

- Structured & non-structured (particle) reactors.
- Solar heating: only direct (required Ts too high for indirect heating).

Principle of the solar thermal fuel production



Solar Tower

Resources
(Natural Gas)
Water, CO_2

Redox chemistries
+ heat

Heat

Heat +
electricity

Chemical
Reactor

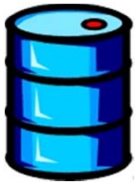
Electrolyzer

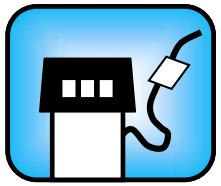
H_2
$CO + H_2$

CH_4, CH_3OH,
Fisher-Tropsch Fuels

Industry
Transportation

Energy Converter
Fuel Cell





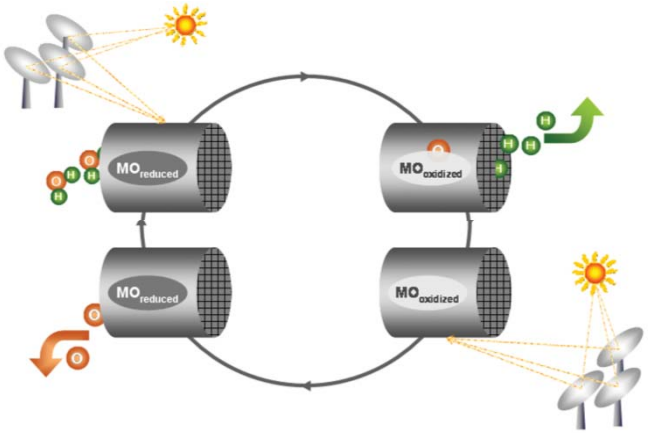
Clean Exhaust

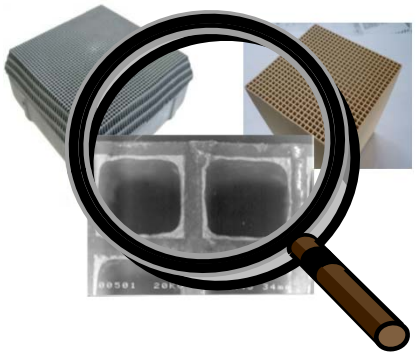
Transportation

Power Production

DLR

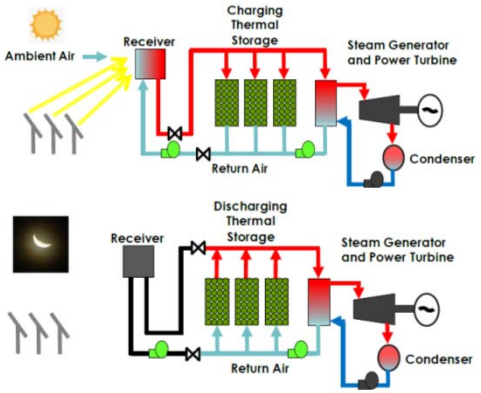
Redox-oxide-based thermochemical cycles - structured ~~receiver~~/reactors / heat exchangers





On Sun

Off Sun



1st Step: Thermal reduction (Regeneration) $MO_{ox} + \Delta H \rightarrow MO_{red} + ½\ O_2$

2nd Step: H_2O / CO_2 Splitting WS /CDS

$H_2O + MO_{red} \rightarrow MO_{ox} + H_2 + (\Delta H)$

$CO_2 + MO_{red} \rightarrow MO_{ox} + CO + (\Delta H)$

Net reaction: $H_2O \rightarrow H_2 + ½\ O_2$

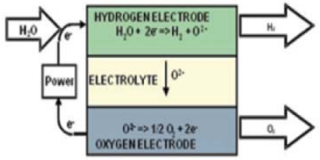
Net reaction: $CO_2 \rightarrow CO + ½\ O_2$

Net effect: Solar Q →Solar Fuels (H_2, syngas)

2nd Step: (Air) Oxidation (AO)

$MO_{red} + ½\ O_2 \rightarrow MO_{ox} + \Delta H$

TR aided by electrical energy: (high T) Solid Oxide (co)electrolysis Cell **(SOEC)** for WS/CDS to H_2/CO.

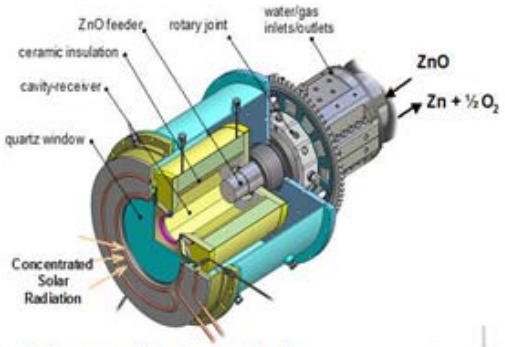


SOEC

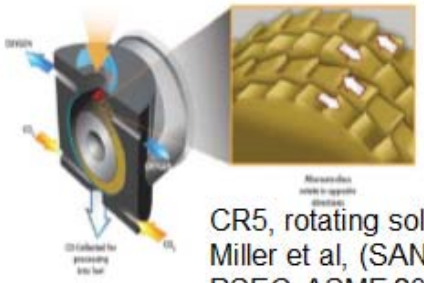
Net effect: Solar Q → ΔH → Q non-solar

Thermochemical storage

Solar receiver/reactor types (particles vs. porous solids; moving vs. non-moving parts)

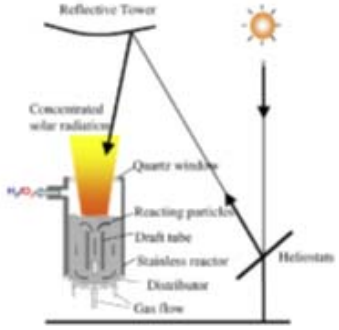


Rotating cavity (powder) Loutzenhiser et al (ETH), Materials, 2010.

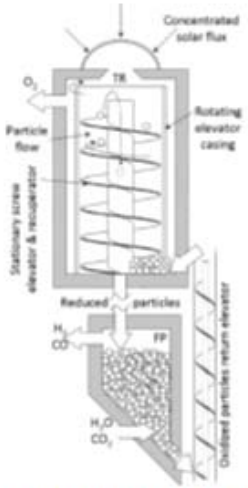


CR5, rotating solid disks Miller et al, (SANDIA) : PSEC, ASME 2006.

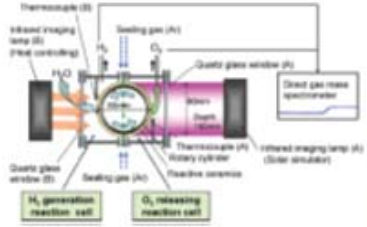
Ceramic honeycombs SOLAIR receiver (DLR), 2004.



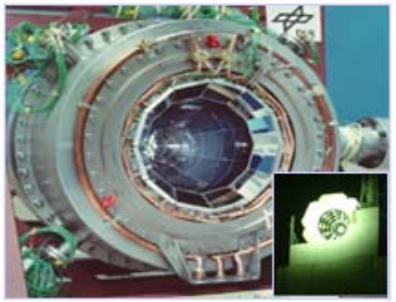
Spouted (powder) bed, Gokon et al (Niigata Univ.), IntJHEn, 2011.



Moving powder bed Ermanoski et al, (SANDIA), JSolEnergyEng 2013.

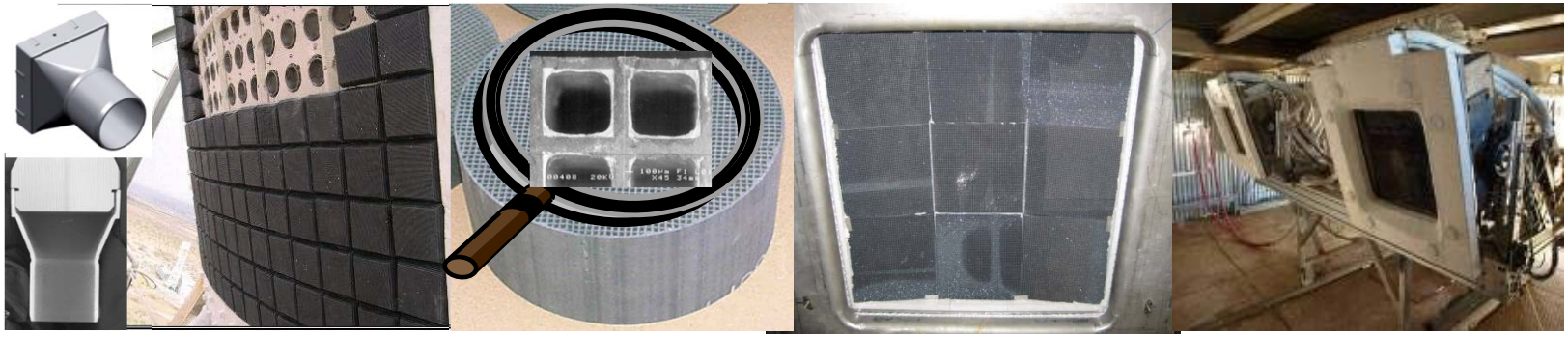


Rotating solid drum Kaneko et al, (Tokyo Univ.), EnFuels 2007.



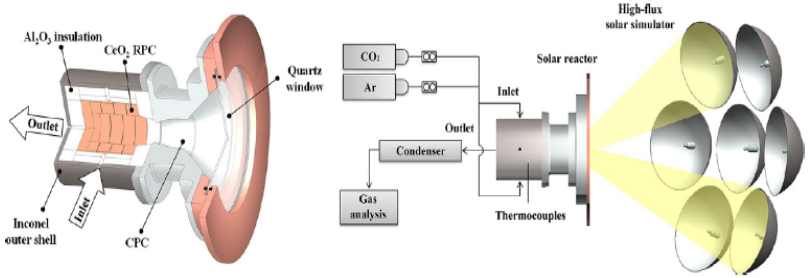
Ceramic foams SOLREF reactor (DLR), 2004.

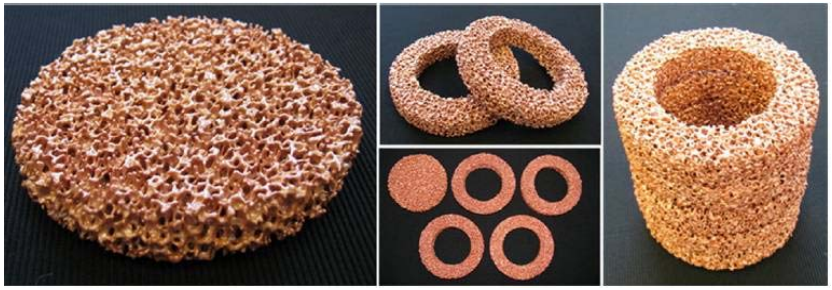
Solar fuels: Solar receiver/reactors based on coated honeycombs:



C. Agrafiotis, M. Roeb, A.G. Konstandopoulos, L. Nalbandian, V.T. Zaspalis, C. Sattler, P. Stobbe, A.M. Steele, Solar water splitting for hydrogen production with monolithic reactor, Solar Energy, 79(4), 409-421, (2005).

From active-material-coated “inert” structural supports to structures made entirely of the active material:

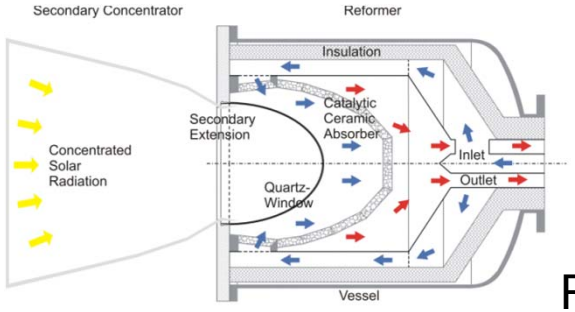




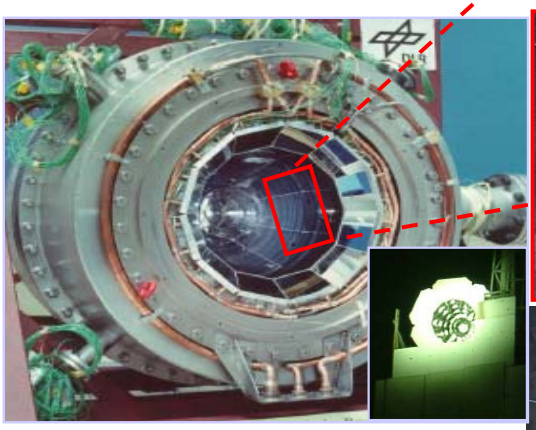
P. Furler, J. Scheffe, M.Gorbar, L. Moes, U. Vogt, A. Steinfeld, Solar Thermochemical CO_2 Splitting Utilizing a Reticulated Porous Ceria Redox System, Energy & Fuels, 26(11), 7051-59, (2012).

Further scale-up: "Convergence" of reactor concepts

Directly heated receiver/reformers (SOLASYS, SOLREF, 1998-2009)



Rh/Al_2O_3 -coated SiC foam



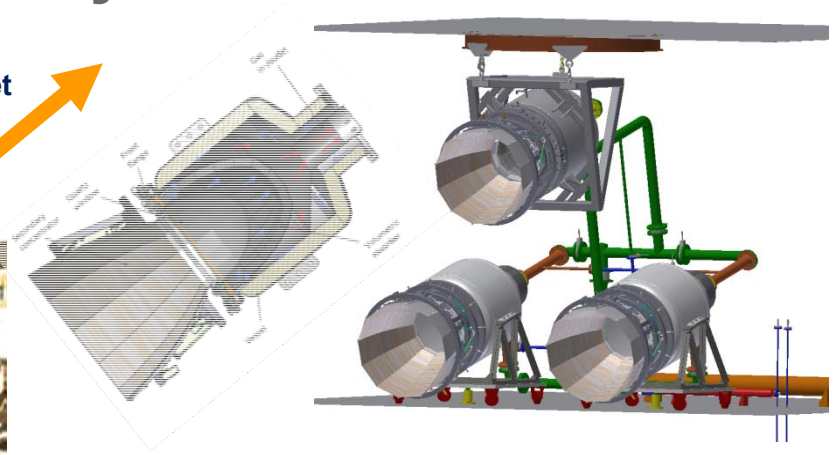
Solar Platform-WIS Israel

Directly heated WS/CDS reactors (HYDROSOL-PLANT, 2012-2017)

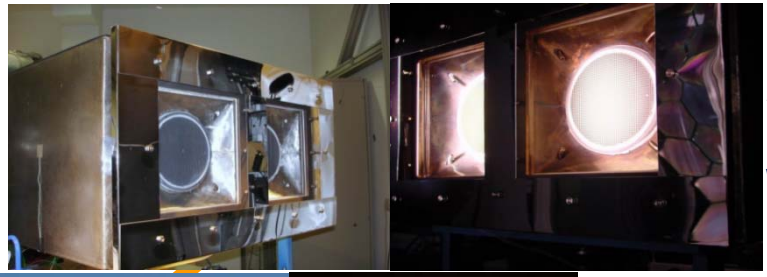
- Domed reactor chamber.
- Assembled of individual foam pieces.
- WS/CDS: "**Redox-oxide-made" foams** (from $NiFe_2O_4$ and CeO_2-ZrO_2); interchangeable with catalyst-coated ones (SMR).

HYDROSOL Technology: Continuous (dual chamber) Solar Receiver / Reactor scalability and evolution

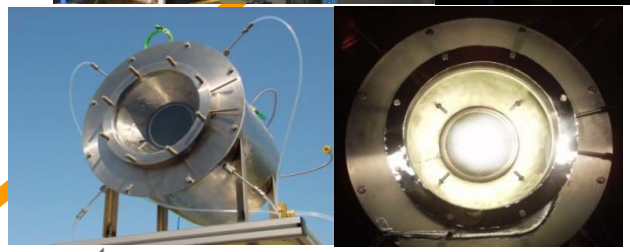
2017: 750 kW_{th}, Almeria, (Schack et al. Solar Energy, 2016,17).



2008: 100 kW, PSA, Almeria, (Roeb et al, Solar Energy, 2011).

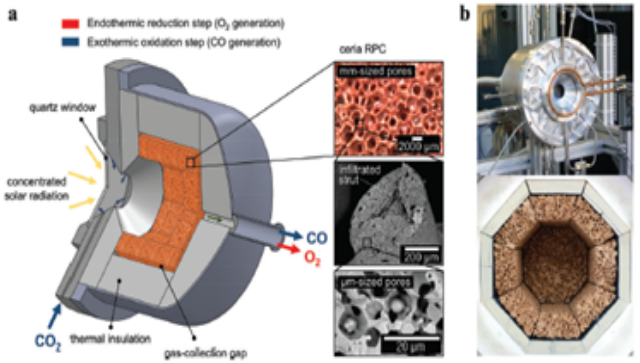


2004: 3 kW, DLR, Cologne, (Roeb et al, WHEC, 2006).



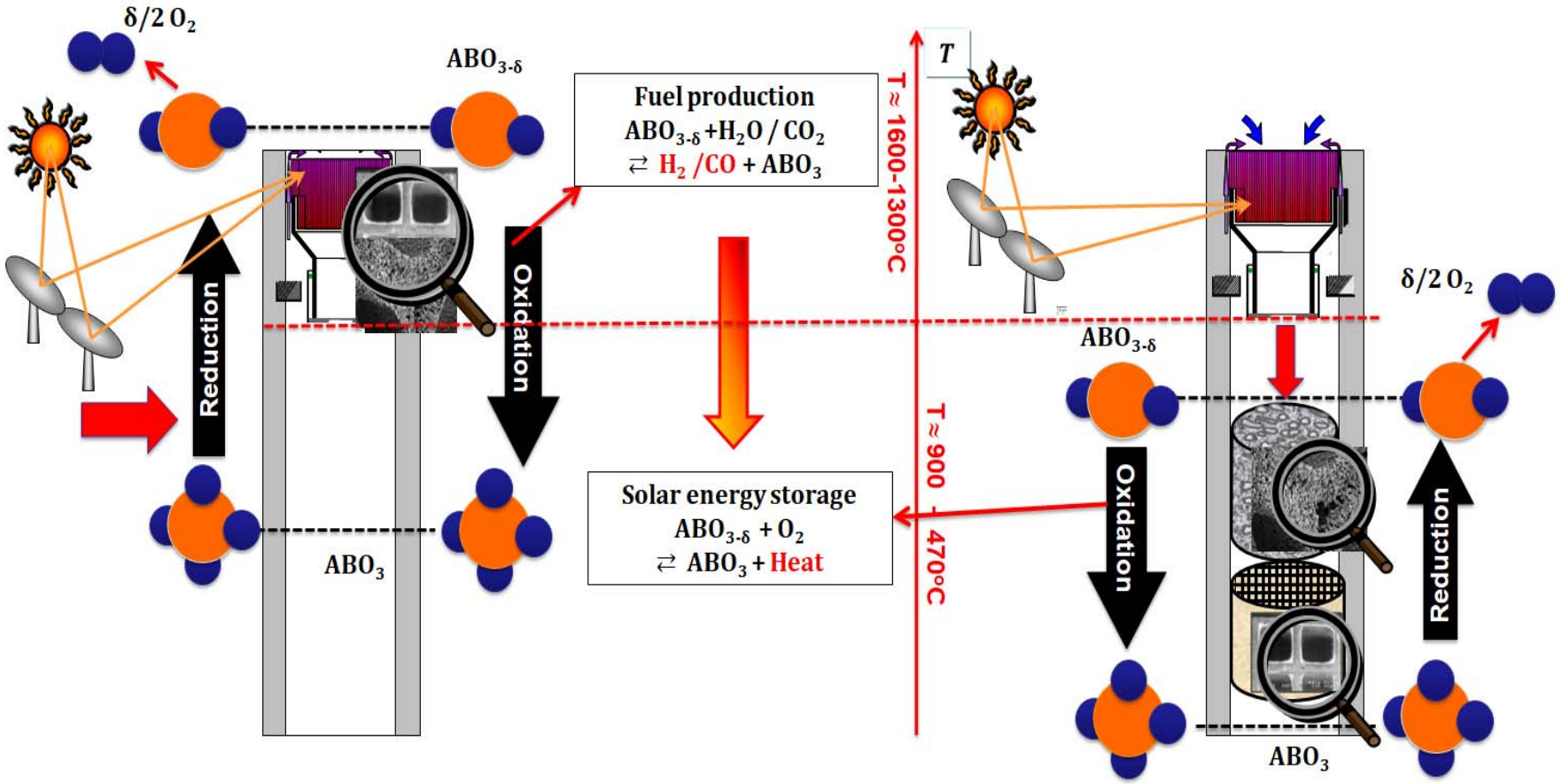
2002: 0.5 kW, DLR, Cologne, (Agrafiotis et al, Solar Energy, 2005).

2017: 50 kW, ETH, Madrid, (Marxer et al, Energ. Envi. Sci.,2017).



DLR

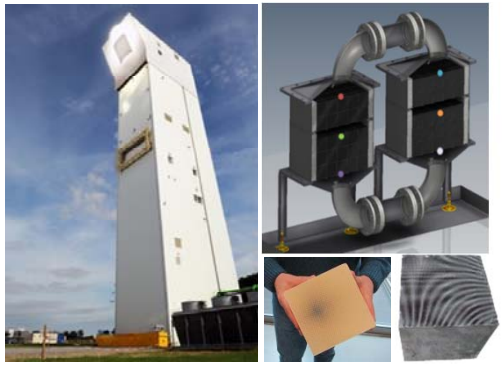
From WS/CDS to TCS
(or from direct heating to allothermal heating)



RESTRUCTURE / STOLARFOAM technology: TCS reactor / heat exchanger scalability and evolution

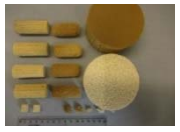
m_{Co3O4} = **88 kg**

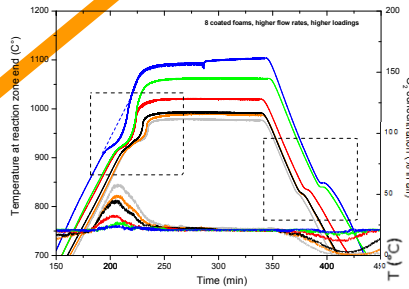
Pilot-scale Co_3O_4 coated cordierite honeycombs

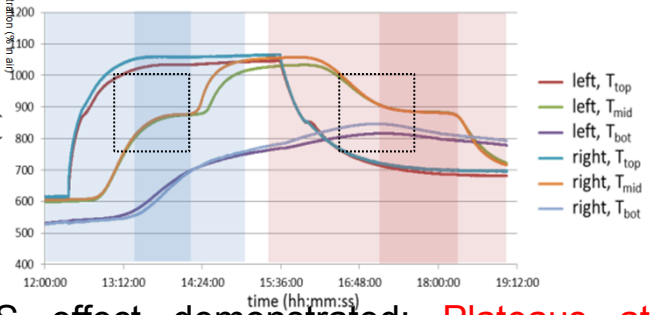


Lab-scale Co_3O_4-made and coated objects (**Pagkoura et al, Solar Energy, 2014, Tescari et al, 2014, Karagiannakis et al, Solar Energy, 2016, Agrafiotis et al, Solar Energy 2014, 2015, 2016**).

m_{Co3O4} = 10-150 g

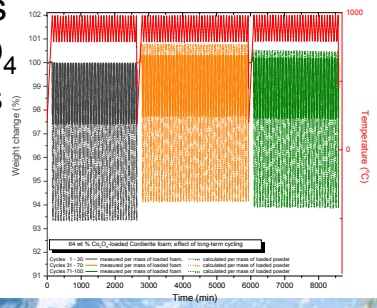






m_{Co3O4} = 200 mg

Powders, mini Co_3O_4 made and coated objects 100 cycles; all Co_3O_4 exploited, no activity loss



TCS effect demonstrated: Plateaus at constant temperature with Co_3O_4-coated honeycombs.High energy density; efficient heat release, cyclic performance without degradation over 15 cycles, structural integrity maintained, no coating spallation (**Tescari et al, Applied Energy, 2017, Singh et al, Solar Energy, 2017**).

Properties of merit required for redox oxide pairs

WS/CDS TCS SOEC

- **Reduction of oxidized oxide state at "reasonable" temperatures**

Under low P_{O2}	Under air	Under applied voltage
• Reactivity of reduced oxide with H_2O/CO_2 • High volumetric/ gravimetric H_2, CO yield	• High ΔH of air oxidation; reversibility • High volumetric energy storage density	• High ionic (oxygen) and electronic conductivity • Reactivity with H_2O and/or CO_2

- **Long-term cycling chemical, mechanical, thermal and dimensional stability**

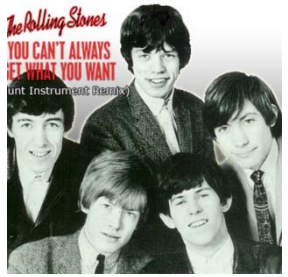
WS/CDS materials
Ferrites $(Ni,Co)Fe_2O_{4-\delta ox}$
Ceria $CeO_{2-\delta ox}$
Perovskites:$La_{1-x}Sr_xAlO_{3-\delta ox}$
T ≈1500-700°C

TCS materials
Co_3O_4 T_{eq}=870°C
$(Fe,Mn)_2O_3$ T_{eq}=970-920°C
Perovskites:$CaMn_{1-y}B_yO_{3-\delta ox}$
$T_{eq}\geq$ 470°C

O_2 electrode materials
LSM-YSZ
Perovskites: LSCF
$La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta ox}$
T ≈ 1000-500°C

Criteria for solar thermal materials/processes selection?

"…You can't always get what you want, but if you try, sometimes you just might find, you get what you need…". The Rolling Stones, 1969.



Want !

CSP-carbon-neutral solar fuels from sun, H_2O and CO_2 but "*…the reactions involved are on the edge of being feasible and practicable…*".

CSP-reactors with high theoretical efficiency.

Redox pair material compositions that can be thermally reduced and split H_2O / CO_2.

Need ?

Hybrid options exploiting similar materials and reactors yet realizable under milder conditions, as a transition path from fossil fuel-based solar-fuels to such produced only by renewable resources?

Technically simpler, viable, pragmatic CSP-reactor concepts attractive for large-scale implementation and demonstration?

Bulk, robust, porous oxide structures from inexpensive raw materials, that can perform cyclic redox operations for extended periods of time? (WS/CDS, TCS, Membranes, SOECs)?

Thank you for your attention!